Investigating and Quantifying CO₂-Fluid-Shale Interactions

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Abstract

Investigating and quantifying the interactions that occur between CO₂ fluids, and shale is becoming increasingly important. These interactions will play a large role when (1) storing CO₂ in hydraulically fractured shale formations, (2) utilizing CO₂ as a hydraulic fracturing fluid, and (3) determining if CO₂ can be an effective agent for enhancing hydrocarbon recovery. Regardless of the reason, as CO₂ is injected into a shale formation, it will interact with shale components (e.g. organic matter, minerals, cations/anions) driving various reactions that will alter the rock properties. The alteration of these properties, such as porosity or permeability, will impact the permanence of CO₂ storage and the effectiveness of CO₂ to work as a fracturing or hydrocarbon extraction agent. To examine these alterations, Marcellus and Utica shale samples were analyzed in the presence of CO₂ and fluid (water). Techniques used include feature relocation scanning electron microscopy (SEM), surface area and pore size analysis using volumetric gas sorption and density functional theory (DFT) methods, and in-situ Fourier Transform infrared (FTIR) spectroscopy. Feature relocation SEM showed little alteration before and after dry and wet CO₂ exposure in the siltitic rich Marcellus Shale (MS-4) sample. However, the carbonate rich Marcellus Shale (MS-4) and Utica Shale (US-1) samples experienced minor etching with dry CO₂ and significant carbonate dissolution and precipitation with wet CO₂. After exposure to CO₂ and water, the Brunauer-Emmett-Teller (BET) surface area of the siltic-rich Marcellus Shale increased while the carbonate rich Marcellus Shale decreased. FT-IR spectroscopy indicates formation and dissolution of carbonate species in hydrated carbonate rich shales which buffer as a function of pH with exposure to CO₂ and pressure. Current in-situ FT-IR results are limited to fully saturated samples or completely dry samples. A new system set up, designed to control relative humidity and allow examination of partially hydrated samples, is presented.

Samples

A: US-1
B: Utica Shale (outcrop)
C: US-P2
D: Utica Shale (Prod. Zone)
E: CO₂ - exposed
F: CO₂ - exposed
G: MS-4
H: Barnett Shale
I: MS-4
J: Barnett Shale
K: Unexposed
L: Barnett Shale
M: Barnett Shale

Instruments

Scanning Electron Microscopy used for feature relocation before and after dry/wet CO₂ exposure.

Surface Area and Pore Size Analysis: Results

US-1

Pore size distribution of US-1 based on CO₂ (left) and N₂ (right) isotherm characterization. BET surface area = 5.8-6.8 (m²/g).

MS-1

Pore size distribution of MS-1 based on CO₂ (left) and N₂ (right) isotherm characterization. BET surface area = 3.7-8.3 (m²/g).

MS-4

Pore size distribution of MS-4 based on CO₂ (left) and N₂ (right) isotherm characterization. BET surface area = 12.1-49.5 (m²/g).

IR Relative Humidity System

A: Gas inlet from cylinders
B: Micro metering valve for dry gases
C: Micro metering valve for wet gases
D: Fluid drip tube
E: Pressure transducer
F: Pressure reader
G: Relative humidity probe
H: Relative humidity reader
I: Gas outlet to sample cell
J: Back pressure diaphragm
K: Back pressure regulator
L: Temperature reader

References